

Kinetic Theory of Gases

Chapter 3

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History of ideal gas law

- 1662: Robert Boyle discovered with changing pressure at constant temperature that product of pressure and volume of a gas at equilibrium is constant, $pV = \text{constant}$ at constant T .
- 1780's Jacques Charles found that ratio of volume to temperature was also invariant when temperature was changed with pressure kept constant, $V/T = \text{constant}$ at constant p
- 1811 Amedeo Avogadro found ratio of volume to amount remained constant with changing amount at fixed pressure and temperature, $V/n = \text{constant}$ at constant p and T .
- 1834 Emile Clapeyron combined gas laws of Boyle, Charles, and Avogadro into ideal gas equation of state,

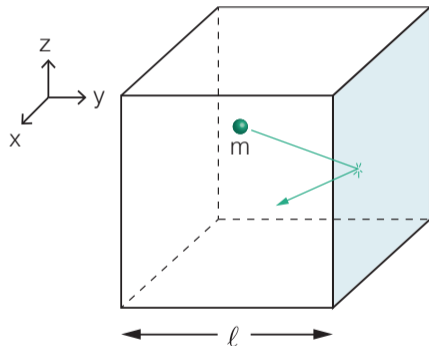
$$pV = nRT$$

where R is gas constant.

Bernoulli's derivation of Boyle's law, $pV = \text{constant}$.

As early as 1738 Daniel Bernoulli proposed a microscopic kinetic explanation of Boyle's law, but only after Clapeyron's work did Bernoulli's kinetic theory gain widespread acceptance.

Bernoulli's derivation

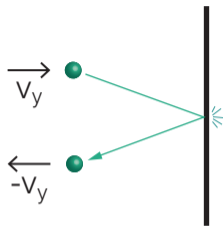


Remember pressure is defined as force per unit area. What is the force of one gas molecule hitting a wall?

Force on wall is momentum change when a molecule hits it.

Force along y is given by ratio of change in momentum to time between collisions.

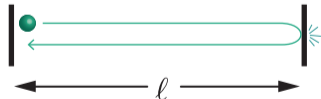
$$F_y = \frac{\Delta p_y}{\Delta t}$$



Linear momentum is conserved in collision with wall

$$\Delta p_y = p_{y,\text{final}} - p_{y,\text{initial}} = (-mv_y) - (mv_y) = -2mv_y$$

Time to travel length of box, hit wall, and travel back is $\Delta t = 2\ell/v_y$



Average force of 1 molecule hitting 1 wall of box is $F_y = \frac{\Delta p_y}{\Delta t} = \frac{-2mv_y}{2\ell/v_y} = -\frac{mv_y^2}{\ell}$

Force of N molecules hitting all walls of the box.

Sum over N molecules hitting one wall is

$$F_{yN} = -\frac{m}{\ell} \sum_{j=1}^N v_{y_j}^2$$

Add **magnitude** (i.e., ignore signs) of all forces on all walls (top, bottom, left, right, front, back)

$$F_{\text{total}} = 2\frac{m}{\ell} \sum_{j=1}^N \underbrace{(v_{x_j}^2 + v_{y_j}^2 + v_{z_j}^2)}_{v_j^2} = 2\frac{m}{\ell} \sum_{j=1}^N v_j^2$$

Define mean square velocity as

$$\overline{v^2} = \frac{1}{N} \sum_{j=1}^N v_j^2 \quad \text{or} \quad N\overline{v^2} = \sum_{j=1}^N v_j^2$$

and write total force on all walls of box as

$$F_{\text{total}} = 2\frac{m}{\ell} N\overline{v^2}$$

Pressure from N molecules inside the box.

Pressure is force per unit area. Total area of box walls is 6 times area of 1 wall: $A_{\text{total}} = 6A_{\text{wall}}$.

$$p = F_{\text{total}}/A_{\text{total}} = F_{\text{total}}/(6A_{\text{wall}}) \quad \text{Substituting previous result: } F_{\text{total}} = 2\frac{m}{\ell}N\overline{v^2}$$

gives

$$p = 2\frac{m}{\ell}N\overline{v^2}/(6A_{\text{wall}}) = \frac{Nm\overline{v^2}}{3A_{\text{wall}}\ell} = \frac{Nm\overline{v^2}}{3V}$$

$V = A_{\text{wall}}\ell$ is volume of box.

Rearranging gives Boyle's law ($pV = \text{constant}$)

$$pV = \frac{Nm\overline{v^2}}{3} = \frac{2}{3}N\left(\frac{1}{2}m\overline{v^2}\right) = \frac{2}{3}N\overline{\epsilon}_k, \quad \text{where } \overline{\epsilon}_k \text{ is mean kinetic energy of molecule}$$

Set $N = N_A$ for 1 mole of gas molecules and $N_A\overline{\epsilon}_k = E_k$ is kinetic energy of 1 mole of gas

$$pV = \frac{2}{3}N_A\overline{\epsilon}_k = \frac{2}{3}E_k \quad \text{compare to } (n = 1) \text{ ideal gas law } pV = RT$$

and we discover

$$E_k = \frac{3}{2}RT$$

Temperature is a quantity derived from energy

The kinetic energy of 1 mole of an ideal gas

$$E_k = \frac{3}{2}RT$$

- Equation reveals true nature of temperature—reflects kinetic energy of atoms and molecules.
- You can't have negative temperatures because you can't have negative kinetic energy.
- Raising temperature of gas increases kinetic energy of gas and vice versa.
- Dividing by N_A we obtain relationship on per molecule basis

$$\bar{e}_k = \frac{3}{2} \frac{R}{N_A} T = \frac{3}{2} k_B T$$

$k_B = R/N_A = 1.38064852 \times 10^{-23}$ J/K is defined as Boltzmann constant.

Average molecular speed

Given

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_B T$$

define root mean square speed, $c_{\text{rms}} = \sqrt{\overline{v^2}}$, and obtain

$$c_{\text{rms}} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}}$$

c_{rms} is related to temperature and molecular mass, m , or molar mass, M

- Average kinetic energy and speed of molecules increases with increasing temperature.
- Average kinetic energy and speed of molecules decreases with increasing molecular mass.

Average molecular speed

Example

Calculate the root mean square speed for a mole of vanillin molecules at room temperature.

Solution

Since Vanillin has chemical formula $C_8H_8O_3$ with a molecular weight of 152.1 g/mol we obtain

$$c_{\text{rms}} = \sqrt{\frac{3R(300 \text{ K})}{152.1 \text{ g/mol}}} \approx 221 \text{ m/s} \approx 500 \text{ mph}$$

If vanillin has such a high speed why does it take so long for the scent to travel across a room?

Maxwell Distribution Laws

Maxwell Distribution Laws

In 1859 James Clerk Maxwell worked out the probability distribution of molecular velocities, $f(\vec{v})$, for gas molecules as perfectly elastic spheres.

Maxwell assumed that distribution of velocities in each direction were uncorrelated, that is, $f(\vec{v})$ can be written as product of 3 independent distributions

$$f(\vec{v}) = f(v_x) f(v_y) f(v_z)$$

He also reasoned that distribution of velocities is independent of direction, implying that $f(\vec{v})$ should only depend on magnitude of velocities,

$$f(v_x) f(v_y) f(v_z) = \phi(v_x^2 + v_y^2 + v_z^2)$$

This is an example of a *functional equation*: an equation in which the unknowns are functions.

How do we solve this functional equation?

$$f(v_x) f(v_y) f(v_z) = \phi(v_x^2 + v_y^2 + v_z^2)$$

Product of functions on left must give sum of their variables as function argument on right.

A function, $f(v_i)$, that satisfies this functional equation is

$$f(v_i) = a e^{-b v_i^2}$$

Putting this function into functional equation gives

$$\phi(v_x^2 + v_y^2 + v_z^2) = a^3 e^{-b(v_x^2 + v_y^2 + v_z^2)}$$

Normalizing Maxwell's distribution for molecular velocities

As the $f(v_i)$ are probability distributions we require them to be normalized,

$$\int_{-\infty}^{\infty} f(v_i) dv_i = 1$$

This leads to $a = \sqrt{b/\pi}$ and

$$f(v_i) = \sqrt{\frac{b}{\pi}} e^{-bv_i^2}$$

Taken together Maxwell's probability distribution becomes

$$f(\vec{v}) = \left(\frac{b}{\pi}\right)^{3/2} e^{-b(v_x^2 + v_y^2 + v_z^2)}$$

Maxwell's distribution law for molecular velocities

From Bernoulli's kinetic theory we learned that $\overline{v^2} = 3k_B T/m$.

This mean square speed should also be obtained from our probability distribution according to

$$\overline{v^2} = \int_{-\infty}^{\infty} (v_x^2 + v_y^2 + v_z^2) f(v_x) f(v_y) f(v_z) dv_x dv_y dv_z.$$

Substituting our normalized solutions for $f(v_i)$ we obtain

$$\overline{v^2} = \int_{-\infty}^{\infty} (v_x^2 + v_y^2 + v_z^2) \left(\frac{b}{\pi}\right)^{3/2} e^{-b(v_x^2 + v_y^2 + v_z^2)} dv_x dv_y dv_z.$$

Evaluating this integral and setting it equal to $3k_B T/m$ yields $b = m/(2k_B T)$. Thus we find

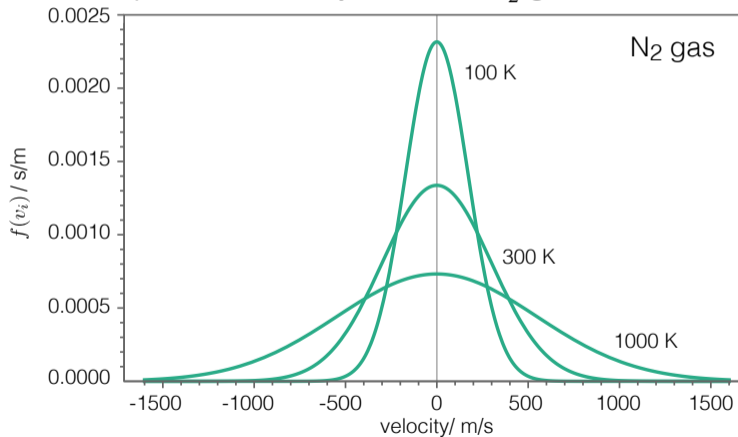
$$f(\vec{v}) = \frac{1}{\sqrt{(2\pi)^3}} \left(\frac{m}{k_B T}\right)^{3/2} e^{-\frac{1}{2}(v_x^2 + v_y^2 + v_z^2)/(k_B T/m)}$$

This is *Maxwell's distribution law for molecular velocities*.

Maxwell's distribution law for molecular velocities

Maxwell's distribution law is a 3D Gaussian distribution centered on $\vec{v} = 0$.

Distribution for one component of velocity vector for N_2 gas at 3 different temperatures.



Maxwell's distribution law for molecular speeds

Maxwell's distribution law for molecular speeds

Speed is magnitude of velocity vector. To get speed distribution transform Maxwell's velocity distribution into spherical coordinates,

$$c = \sqrt{v_x^2 + v_y^2 + v_z^2}, \quad \cos \theta = \frac{v_z}{c}, \quad \tan \phi = \frac{v_y}{v_x}.$$

With this change of variables we find

$$f(\vec{v}) = f(c, \theta, \phi) = \frac{1}{\sqrt{(2\pi)^3}} \left(\frac{m}{k_B T} \right)^{3/2} e^{-\frac{1}{2}c^2/(k_B T/m)}$$

This is independent of θ and ϕ so if we put it into the normalization

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} f(c, \theta, \phi) c^2 dc \sin \theta d\theta d\phi = 1$$

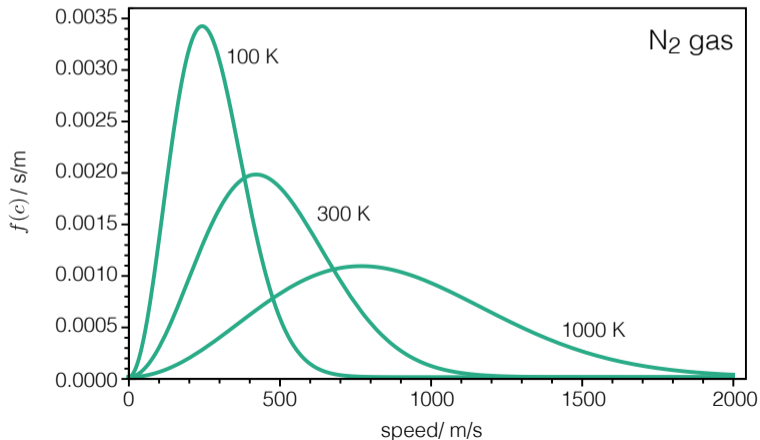
we can integrate away θ and ϕ and obtain

$$f(c) = \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_B T} \right)^{3/2} c^2 e^{-\frac{1}{2}c^2/(k_B T/m)}$$

*Maxwell's distribution law
for molecular speeds.*

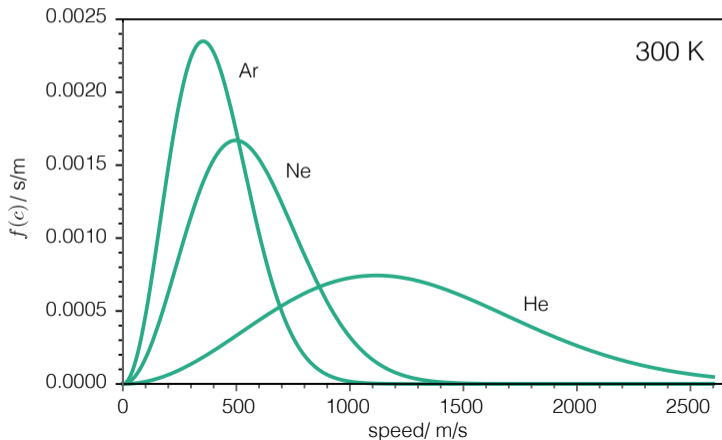
Maxwell's distribution law for molecular speeds

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Maxwell's distribution law for molecular speeds

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Kinetic Theory of Gases Simulation

Mean speed

With Maxwell's distribution law for molecular speeds

$$f(c) = \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_B T} \right)^{3/2} c^2 e^{-\frac{1}{2}c^2/(k_B T/m)}$$

we can calculate the mean speed

$$\bar{c} = \int_0^{\infty} cf(c)dc = \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_B T} \right)^{3/2} \cdot \frac{1}{2} \left(\frac{2k_B T}{m} \right)^2$$

which simplifies to

$$\bar{c} = \sqrt{\frac{8k_B T}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$$

Note that mean speed, \bar{c} , is smaller than root mean square speed, c_{rms} .

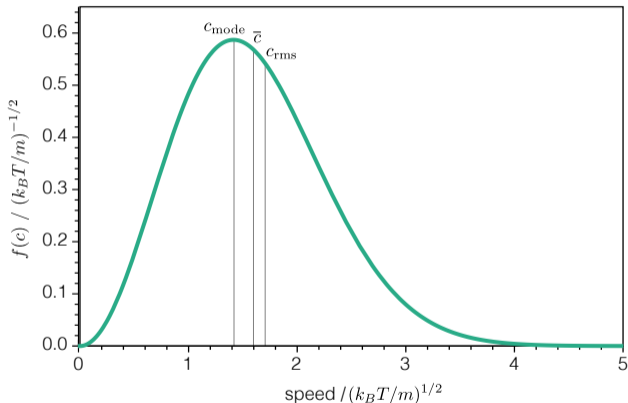
Most probable speed

$$f(c) = \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_B T} \right)^{3/2} c^2 e^{-\frac{1}{2}c^2/(k_B T/m)}$$

To calculate most probable speed need to find c value where $f(c)$ is maximum.

Set $df(c)/dc = 0$, solve for c to obtain

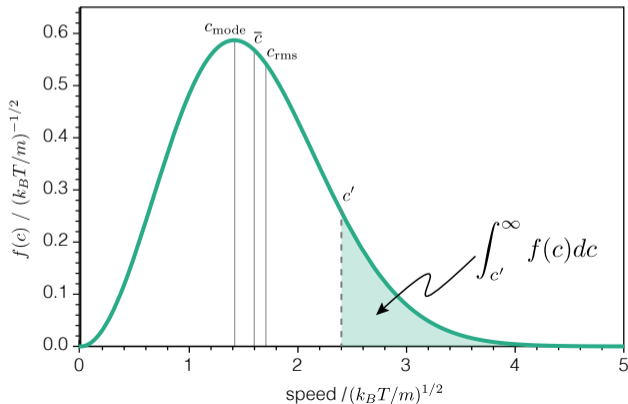
$$c_{\text{mode}} = \sqrt{\frac{2k_B T}{m}} = \sqrt{\frac{2RT}{M}}$$



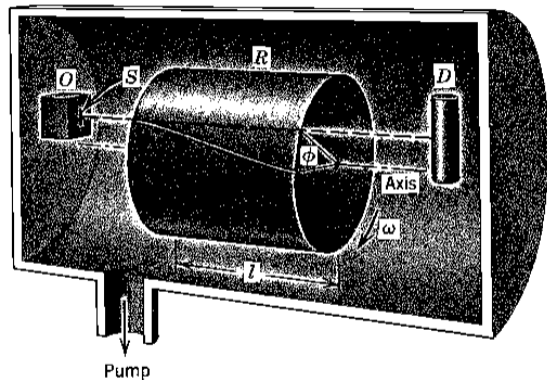
Fraction of molecules with speeds between c_1 and c_2 .

Fraction of molecules with speeds between c_1 and c_2 is obtained by integrating Maxwell speed distributions between these two limits,

$$\frac{\delta N}{N} = \int_{c_1}^{c_2} f(c)dc$$

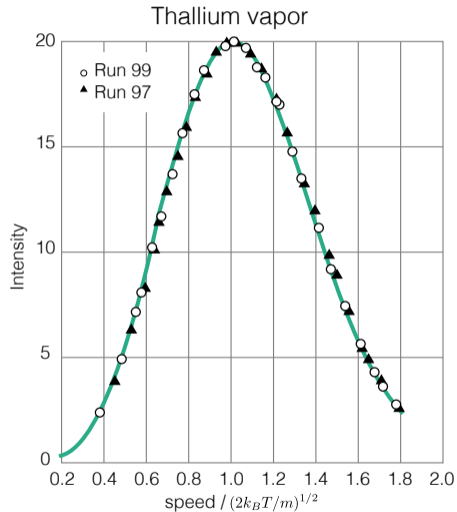
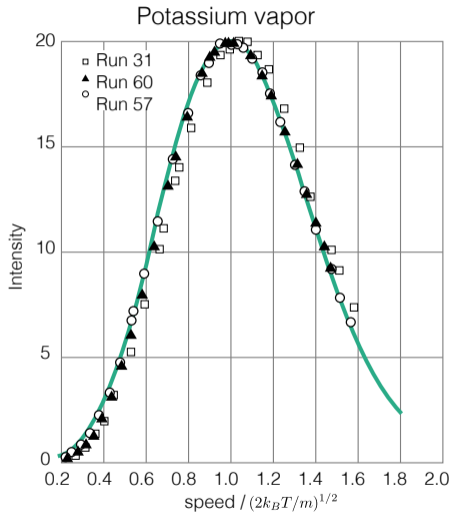


Miller and Kusch experiments



- In 1955 Miller and Kusch published first convincing measurements of speed distribution for K and Tl atoms in gas phase.
- For each fixed rotation speed only molecules with a small range of speeds can travel from the furnace to the detector.
- With dimensions given in instrument diagram the selected speed is $v_0 = \omega l / \phi$.
- Measuring intensity as a function of rotation speed gives the atomic speed distribution.

Miller and Kusch experiments



Miller and Kusch experiments

Beam	Run	Temperature deg K	Oven pressure in mm of mercury	Velocity of I_{\max} in m/sec	
				From oven temp	From exp distr
K	57	466 ± 2	4.5×10^{-3}	628 ± 2	630 ± 3
K	60	544 ± 3	1.2×10^{-1}	678 ± 3	679 ± 3
K	31	489 ± 2	1.4×10^{-2}	644 ± 2	682 ± 3
Tl	99	870 ± 4	3.2×10^{-3}	376 ± 1	376 ± 2
Tl	97	944 ± 5	2.1×10^{-2}	392 ± 1	395 ± 2

Distribution of kinetic energies

Homework

Given

$$f(c) = \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_B T} \right)^{3/2} c^2 e^{-\frac{1}{2}c^2/(k_B T/m)}$$

derive the distribution of kinetic energies,

$$f(\epsilon_k) = \frac{2}{\sqrt{\pi}} \left(\frac{1}{k_B T} \right)^{3/2} \epsilon_k^{1/2} e^{-\epsilon_k/(k_B T)}$$